STUDY OF METAL HYDRIDES AND THEIR APPLICATION IN HEAT PUMPING

by

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CERTIFICATE

It is certified that the work contained in the thesis entitled "STUDY OF METAL HYDRIDES AND THEIR APPLICATION IN HEAT PUMPING" by Manoj Kumar has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

1 2 94

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ABSTRACT

To meet the increasing energy needs and to optimize the use of fossil fuel, new sources of energy were developed. However all of these sources are not safe and easy to use. Out of these hydrogen is an important source of energy. It can be stored in large amount in metal hydrides to transport and use safely. The basic property by which metal hydrides store hydrogen and release it on heating is of importance. Enthalpy of formation play an important role in stability of these hydrides and intermetallic compounds. Only those hydrides are stable for which ΔH is negative. Partial replacement of metal hydrides with metal like (V / Cr / Mn / Ni) gives pronounced effect on the stability.

In present work,enthalpy of formation of various compounds and hydrides of Ti-Fe-H system is calculated using Fortran Programming and effect of partial replacement of Fe by (V / Ni / Ti / Cr) on stability has been studied theoretically.

The absorption and desorption of H_2 by intermetallic is associated with release & absorption of heat energy. One can think of using therefore, metal hydrides to pump heat from one location to other easily. An attempt therefore has been made to study the feasibility of indigenously developed Mischmetal based intermetallic for heat pumping application.

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CHAPTER 1

INTRODUCTION :

These days, in environment conscious world, there is hue and cry to save the environment, control the pollution and optimize the use of conventional sources of energy in order to save the future generation from suffering of harmful effects. With the development, need of energy is increasing day by day. Things which were considered earlier as luxury have become necessity today. There is need to develop new energy sources in order to accommodate the rising energy needs. Keeping with this line, scientist of the world have developed nuclear energy and non-conven~~tional~~ient energy sources like wind, tidal, solar, wave etc. But these sources have not yet become very popular because techniques to use these sources are either very expensive or not very convenient. But with time, when cost of conventional energy increases new sources will become competitive. Further to save the earth from pollution and ozone layer depletion new sources will become popular.

Unlike oil and gas, the alternative non-conventional sources are site specific. Energy generated from them need to be transmitted and distributed after converting into suitable form. In general, primary thermal and mechanical energy is converted into electricity and transmitted to the user-centers. But for some applications such as aviation this method is not suited at all. Ideally the secondary fuel should have total use cycle which is economic, energy efficient, safe and environmentally acceptable.

In addition it should be :-

(i) derivable from abundant and renewable resources

(ii) easily storable and movable over long distances

(iii) safer in wider range of applications.

The alternative fuels are either liquid hydrocarbons, ~~methane~~, methanol, ethanol and hydrogen gas.Of these, synthetic liquid hydrocarbons are very expensive because of heat cost and coal requirement. It's only advantage lies in it's offering continuity of existing petrofuel distribution system. But this is only temporary advantage. Nevertheless it is open to the same objection as natural petroleum with regard to environment pollution. The production of methane, methanol and ethanol is also dependent on the availability of raw material and unfavorable energy balance. In this view it is doubtful if any one of these can be produced on a large scale to match the usage of the petroleum.

In contrast hydrogen possess several unique advantages over the other alternative and satisfies practically all the criterion for ideal secondary fuels enumerated earlier. Hydrogen is a promising medium for both, energy transmission and storage. It is essentially non polluting.Since major byproduct of combustion being water (H_2O). Further hydrogen has the highest energy density per unit weight of any chemical. This can be seen from table(1.1)[4].It has a diversified number of uses ranging from combustion engine to fuel cells. One of the greatest limitations in exploitation of hydrogen as a fuel however, appears to be difficulty in storing it economically and conventionally. Hydrogen can be extracted from

TABLE 1.1

COMPARISION OF THE ENERGY DENSTY IN VARIOUS FUELS

POWER SOURCE	ENERGY DENSITY (WATT HOUR/KG)	CONVERSION EFFICIENCY	NET WATT HOUR/KG
Pb/acid battery	30	70	21.0
Present	30	70	21.0
Advanced	50	70	35.0
Li/MS battery	150	70	105.0
$FeTiH_{1.7}$	516	30	154.0
Mg_2NiH_4	1121	30	336.0
MgH_2 (10% Ni)	2555	30	767.0
Gasoline	12880	23	2962.0
Gaseous H_2 (100 atm pr.)	33900	30	10170.0

fossils fuels and /or water. The most common method of storing hydrogen is in gaseous form in cylinders at high pressures. But this gives problem of hydrogen embitterment and diffusion leading to certain amount of risk. This method is not very safe. Other methods, in use to store hydrogen, include absorption by metal hydrides.

Metal hydrides are ~~chemical~~ compounds of metal and hydrogen. Hydrogen is stored safely inside the metal itself in large quantities. The amount of hydrogen is greater than either gaseous or liquid storage. The major difficulty, however lies in the weight and cost of hydriding materials.

Hydrogen storage density of hydrides often exceeds the density of liquid hydrogen. The best example of such hydride is water itself. In which partial hydrogen density is 110 Kg/m^3 at 20^oK. The relative partial hydrogen density of some hydrogen compounds is shown in table 1.2[1].

Hydride formation reaction is reversible. Also at a given temperature, in ideal situation, the absorption (formation of hydrides) and desorption (release of hydrogen) take place at nearly the same pressure. Practically, however the absorption and desorption pressures are not the same at a given temperature. This effect is called hysteresis. The temperature for which the absorption and desorption take place at atmospheric pressure may be very different for different hydrides. The suitability of an intermettalic depends on factors such as structure, diffusion rate of hydrogen during charge and discharge and enthalpy of hydride formation.

TABLE 1.2

COMPARISION OF HYDROGEN CONTENTS IN VARIOUS HYDROGEN COMPOUNDS

COMPOUND	MOLECULAR WEIGHT (Kg/Kmole)	NO. OF ATOMS PER UNIT VOLUME $\times 10^{-28}$ (m^{-3})	PARTIAL DENSITY OF HYDROGEN (Kg/m^3)
H_2O	18.0	6.7	111
H_2SO_4	98.1	2.2	36
liqCH_4	16.0	6.3	105
liqH_2	2.0	4.2	71
TiH_2	49.9	9.2	153
$LaNi_5H_6$	438.5	5.3	88
$TiFeH_{1.95}$	105.7	6.2	101

1.1)CHARACTERISTICS OF METAL HYDRIDE SYSTEM :

The reaction of hydrogen with metal (M) to make hydride $M H_x$ is mostly exothermic and it can be written as[4]

$$M + \frac{X}{2} H_2 = M H_x + \Delta H$$

The reverse reaction is desorption process and forward reaction is absorption process. Reverse reaction is endothermic in nature and external heat is to be supplied for desorption process.The absorption and desorption process of metal- hydride system are studied by means of pressure-composition isotherm in fig 1.1[4].It is plot of pressure and composition at various temperature . The initial steep slop corresponds to hydrogen going into solid solution and this single phase region is a denoted as α-phase. The position where the curve begins to change slope onthe P-C-T diagram denotes the appearance of a metal hydride of β-phase. Due to varied degree of solubility of hydrogen in metals,the resulting metal hydrides sometime become non-stoichiometric. In second phase, hydrogen pressure remains constant and a plateau results, as more hydrogen is added. The plateau continues as long as there are two distinct phases as required by Gibb's phase rule.

$$F = C - P + 2$$

Where

F = degree of freedom

C = number of compositions

P = number of phases

The effect of temperature is shown in fig 1.1[4].In general, as the temperature is increased, the miscibility gap tends to narrow

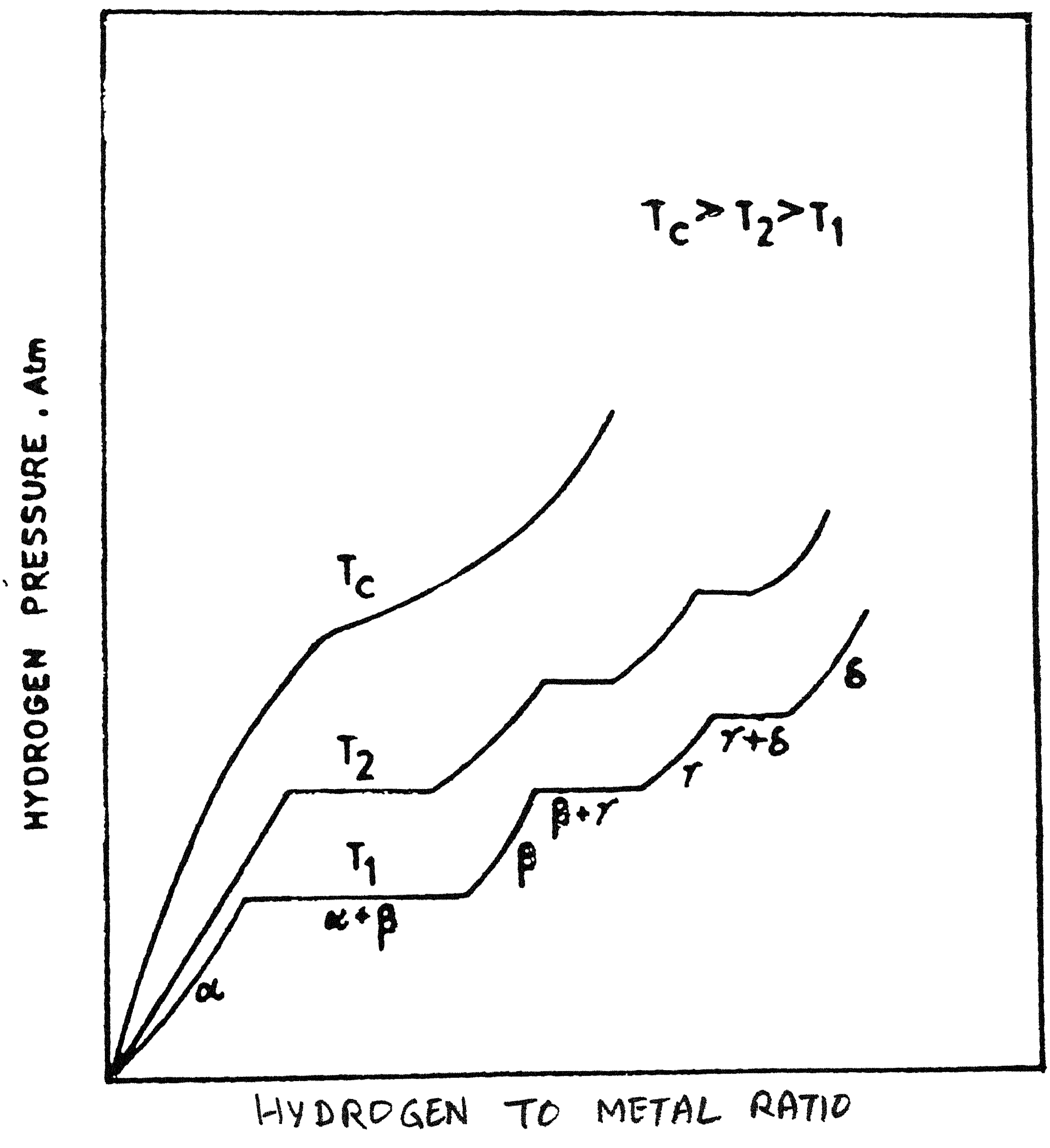

Fig 1.1 PRESSURE VS HYDROGEN TO METAL RATIO ISOTHERM

and gap disappears and α-phase converts continuously into β-phase. Yet another hydride phase(γ) may be formed, for which a higher plateau pressure results.

Plateau pressure which varies strongly with temperature can be described approximately in a limited temperature range by [1]

$$\ln p_{H_2} = - \frac{\Delta S}{R} + \frac{\Delta H}{RT}$$

Where

ΔH = change in enthalpy/ mole of hydrogen

ΔS = change in entropy/ mole of hydrogen

R = universal gas constant

When ΔS and ΔH are taken to be temperature independent in the limited temperature range considered, a plot of ln p vs 1/T (fig 1.2)[4] yields the values for ΔS and ΔH. Slope of curve gives ΔH and intercept with 1/T axis gives ΔS. The negative entropy effect predominantly determined by difference between entropy of hydrogen in gaseous state and in hydride (solid state). Since the later energy consideration is relatively small, $-\Delta S$ will not be much different from entropy contained in the gas which is about 31 calories/degree mole H_2 at one atm. at room temperature.

The sequence of elementary steps which occur during absorption of hydrogen with in a single phase region of solubility is

$$1/2\ H_2 \xrightarrow[\text{Trasport upto surface}]{(1)} 1/2\ H_2\ \text{(Surface)}$$

$$\xrightarrow[\text{Chemisorption}]{(2)} H \xrightarrow[\text{surface migration}]{(3)} H\ \text{(entering site)}$$

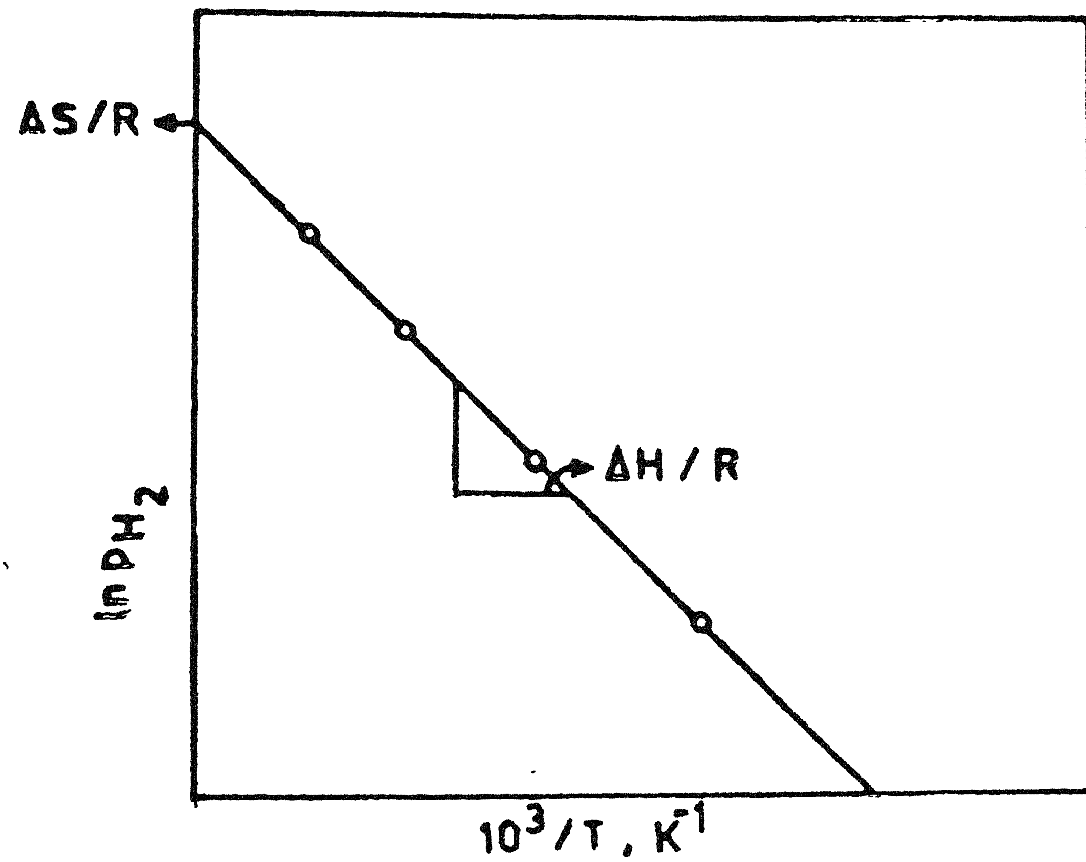

Fig 1.2 VARIATION OF PRESSURE WITH TEMPERATURE

$$\xrightarrow[\text{absorption transition}]{\text{(4) Chemisorption to}} [H] \text{ (adjacent to surface) } \xrightarrow[\text{(bulk)}]{\text{(5) Solid diffusion}} [H]$$

The energy required to break hydrogen molecule into atom is equal to 104.20 Kcals/mol H_2 .

Desorption is reverse of the above sequence with the same steps as for absorption. Step (3) may not be necessary for some solid/H_2 system. The above sequence is limited to reaction occurring under isothermal conditions.

The hydrogen saturated solid and hydride phase (α and β) co-exist in the plateau region. The sequence of steps can be represented as

$$1/2\ H_2 \xrightarrow{(1)} 1/2\ H_2\text{(surface adsorption)} \xrightarrow{(2)} H \xrightarrow{(3)} H \xrightarrow{(4)} [H]$$

$$\xrightarrow{(5)} \text{Interface} \xrightarrow{(6)} [H] \text{ Hydride}$$

Diffusion (step 5) of hydrogen presumably occurs through the hydride to the internal interface where the phase transformation is initiated (step 6). Any of these steps may be slow and will determine the kinetics of the reaction for a given system. In various solubility ranges at different temperatures and pressures the rate of determining step may be different as well.

1.2) HYSTERESIS :

Many metal hydrides show hysteresis effect (absorption and desorption occur at different pressures) at different temperatures as shown in P-C-T diagram for absorption-desorption process (fig 1.3)[4]. The cause of hysteresis is not fully known yet. It is

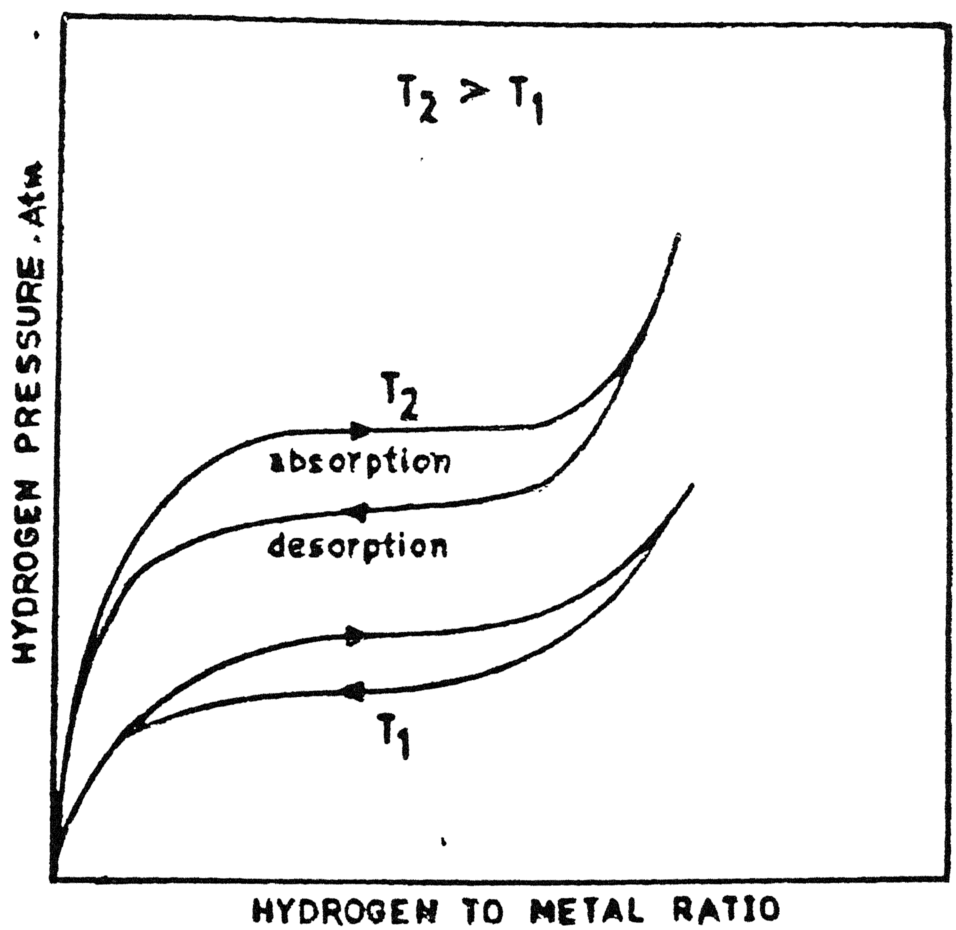

Fig 1.3 HYSTERESIS PLOT OF HYDRIDES

believed that increase in lattice parameters (expansion effect) on hydriding play a vital role. An isothermal cycle of absorption-desorption is initiated by equilibriating gaseous hydrogen with the metallic sample at increasing pressures. The solid expands due to interstitial occupancy of hydrogen (α-phase) as a function of increasing hydrogen gas pressure. As a result micro-regions of the remaining unfilled interstitial sites come in a state of increasing compressive strains, as hydrogen proceeds until β-phase starts developing. Thus the α-phase is subjected to plastic deformation at the micro-level due to compressive stresses during hydrogen absorption and initiation of β-phase precipitation. The system is henceforth in two phase region now, further absorption only increases the amount of β-phase at cost of α-phase maintaining a constant gas pressure (plateau region). The specific volume of β-phase is considerably lower than α-phase, causing severe macro-strains. The corresponding stresses even exceed the fracture strength of bulk sometimes. In general, the original material is overall brittle to some extent. The brittleness is further enhanced by hydrogenation and the solid crumbles into fine powder in the two phase region. The strain is high in the β-phase due to large volume change, that causes localised plastic deformation and develops residual compressive stresses. After α-phase is converted into the strained β-phase further hydrogen can be introduced by increasing the gas pressure again. The β-phase matrix is now under increasing compressive stress in the micro region, similar to the α-phase where the interstitial sites are progressively filled.

Hysteresis becomes apparent in desorption as the boundary of the two phase ($\alpha+\beta$) region is approached. During hydrogen removal the β-phase matrix is increasingly relieved of compressive stresses. This causes the desorption isotherm pressure to drop below plateau found during the absorption cycle. As one approaches the two-phase boundary the β-phase progressively get unstrained.The onset of α-phase precipitation actually contributes in the removal of strains. The β-phase progressively disappears in the two-phase region. Subsequently the equilibrium pressure decreases as the hydrogen is removed from the α-phase. The cycle is completed when hydrogen is removed completely. The degree of hysteresis in a metal-hydrogen system is affected such that it is more pronounced in dynamic than inconventional static tests. Hysteresis reduces the efficiency of hydrogen storage system.

1.3) SURVEY OF HYDRIDES (BINARY AND TERNARY)[4] :

The binary compounds of hydrogen with Boron Gallium and other elements of the 4^{th} to 7^{th} main groups of the periodic table are gaseous/volatile. For example CH_4, NH_3, H_2O and HCl. The halogen hydrides when brought into water, form a positive univalent ion of hydrogen. The hydrides AlH_3, SnH_4 and the germanium hydrides are typical molecular metal hydride. They have a high degree of volatility and a low melting point and are thermally unstable.

The binary compounds of the transition metals, if they combine with hydrogen at all, form metallic hydrides. These hydrides do not always have composition fixed by stoichiometric

ratio. The metals forming such hydrides often first incorporate hydrogen purely in solid solution, without change of crystal structure, although there is some expansion of the crystal lattice. With many metals however, a structural transformation sets in when the amount of hydrogen taken up exceeds a certain concentration. Since this is associated with a discontinuous change in properties it is considered that compound is formed. These metallic hydrides are usually very hard and brittle.

A hydride formed from a binary disordered alloy can be considered as a solid solution of two binary hydrides. For such cases there is only a small difference from the hydride of single metal. A by-hydride formed from an ordered compound, however for example $LaNi_5H_6$ formed from $LaNi_5$, generally has no relation at all to the binary hydrides of the constituents La and Ni. Since these hydrides are formed by absorption of hydrogen at room temperature, where diffusion of La and Ni atom is negligible, the crystal structure of hydride can be derived from that of the original compound by relatively small changes in the La and Ni position. As a matter of fact the lattice has simply to expand to accommodate the hydrogen. The system will show binary behavior e.g.

$$LaNi_5 + 3H_2 \longrightarrow LaNi_5H_6$$

For compounds that absorb hydrogen at high temperature for instance above $300^{o}C$, the diffusion of the metal atom may become possible leading to ternary behavior e.g.

$$3\ Zr_2Cu + 4.75\ H_2 = 5\ ZrH_{1.9} + ZrCu_3$$ [1]

1.4) CHARACTERISTICS OF SOME IMPORTANT INTERMETTALIC HYDRIDES :

(a) AB_5 Compounds :

These hydrides have equilibrium pressure of few atmospheres at temperature upto 100°C, low hysteresis and easy activation in the initial cycle. However both the metallic constituents of the hydrides are very expensive and hence increase the overall cost. AB_5 family exhibits hexagonal or orthorhombic structure. $LaNi_5$ is most important member of this family. It'S reaction with hydrogen is

$$LaNi_5 + 3H_2 = LaNi_5H_6$$ [4]

Plateau pressure at room temperature has been found to be equal to 2.2 atmosphere. Ni addition decreases the stability of rare earth hydrides and improves the capacity of hydrogen absorption. To reduce the cost Ni can be replaced by Al upto some extent. Material is then characterized by lower decomposition pressure without impairing the kinetics of the hydrogen carrying capacity. Replacement of Ni by Pd, Co, Fe, Cr, Ag, Cu, In, Sn and Ga bring down the plateau pressure in all cases except for Pd. However these substitutions decrease the absorption capacity.

(b) AB Compounds :

These intermettalic store hydrogen at the low cost. These materials have equilibrium pressure of a few atmospheres at temperature upto 100°C. Fe_2Ti and FeTi are main compounds. Fe_2Ti does not absorb appreciable amount of hydrogen. For FeTi to react with hydrogen at practical rates reversely, it is necessary to activate the material. The activation is accomplished by out gassing the alloy at 300°C first and contacting it with hydrogen

at a pressure of one atm. later.

Unlike the AB_5 system the reaction kinetics of AB compound is only practically controlled by heat transfer, consequently the chemical reaction rates are of much more significance than heat transfer capability.

The Fe-Ti-H system exhibits pronounced hysteresis effect. Partial replacement of iron by Mn leads to $TiFe_{1-x}Mn_x$ type of intermettalic. The hydrogen to metal ratio for x=0.7 slightly exceeds 1.0.[4]

(c) AB_2 Compounds :

These hydrides posses high hydrogen storage capacity and show resistance to impurities. However high thermal stability has resulted in their limited use.

AB_2 compounds exhibits either cubic C15 or hexagonal C14 structure. Both of these structures have such interstices that are all formed by tetrahedra. As a consequence the hydrogen absorption increases the size of the unit cell without changing the structure. Main compounds of this group are ZrB_2, $ZrFe_2$ etc.

(d) AB_3 Compounds :

Many of the intermettalic of the types AB_5, AB_2, AB_3 are closely related to each other structurally. For example AB_3 structure. While one third of the A atoms have environment identical with those of A atoms of the AB_5 compounds, two third of the A atoms have coordination similar to that found in AB_2 systems. Therefore AB_3 structure can be represented as

$$AB_3 = 1/3\ (AB_5) + 2/3\ (AB_2)$$

The AB_3 compounds form quit stable hydrides of the type $AB_3H_{4.7}$ and exhibit little or no hysteresis. The maximum number of hydrogen atoms by AB_3 formulae united is reported in Er Co_3 system. In this case a composition approaching to the theoretical maximum ($ErCo_3H_{5.5}$) is achieved. Study shows that these materials absorb high amount of hydrogen.

As already pointed out earlier La-riched based intermettalic are very expensive because of high cost of both Ni and La. Hence to reduce the cost of these intermettalic attempts have been made to replace La and Ni with other metals. Thus Mischmetals has been substituted for La. Composition of Mischmetal is given in table 1.3[4]. It is relatively cheap material and does not reduce the advantages of $LaNi_5$ badly.

1.5) PRESENT WORK :

Enthalpy of absorption and desorption of metal hydrides is very much important, as this controls the stability of hydrides. In present work therefore attempts have been made to

(1) calculate the enthalpy of formation of few binary, ternary and quaternary hydrides based on FeTi. Fortran computer programming was used to calculate the enthalpy.

(2) study the possibility of heat pumping using metal hydrides.

TABLE 1.3

COMPOSITION OF MISCH METAL

ELEMENT	ATOMIC WEIGHT	ATOMIC(%)	Wt.% COMPOSITION
Cerium, Ce	140.12	32.9	41.9
Lathanum, La	138.91	22.0	27.1
Neodymium,Nd	144.24	10.2	13.0
Praseodynium,Pr	140.91	-	-
Iron, Fe	55.85	34.6	17.0
Impurities	-	-	1.0

CHAPTER 2

CALCULATION OF ENTHALPY OF FORMATION OF METAL HYDRIDES

Heat of formation of alloys is of great importance. It can be described in terms of a single atomic model. This relatively simple atomic model gives a complete account of the sign of the heat of formation, ΔH of a wide variety of alloy system.

The basic assumption in this model is that the atomic cells of the two constituent metals in the alloys are to a first approximation identical to the atomic cells of the phase metal. The heat of formation alloying is then due to the change in the boundary conditions at the contact surface of the dissimilar cells in the alloy. The energy effects are described by the two terms
(1) a negative energy term arising due to difference in chemical potential($\Delta\Phi^*$) between the two types of the atoms in an alloy
(2) positive energy resulting due to the discontinuity in the density of electrons(Δn_{ws}) at the boundary between dissimilar atomic cells.

The enthalpy of formation, ΔH of an alloy of two transition metals can be written as

$$\frac{\Delta H}{N_o} = f(C^s)\ g\ [-ep(\Delta\Phi^*)^2 + Q_o\ (\Delta n_{ws}^{1/3})^2]$$

where

N_o = Avogadro number

e = elementary charge

$\Delta\Phi^*$ = difference in chemical potential for electron at two types of atom.

Δn_{ws} = discontinuity in the electrons density at the boundary between dissimilar atomic cells.

$P = 0.147\ V^{-1}\ cm^{-2}\ (du)^{-1/3}$

$Q_o = 9.4\ e\ V^2\ /\ (du)^{2/3}$

where

du stands for density units (number of electrons per unit volume)

$\Delta\Phi^* = \Phi^*_A \sim \Phi^*_B$

$\Delta n^{1/3}_{ws} = n^{1/3}_{A_{ws}} \sim n^{1/3}_{B_{ws}}$

$$f(C^s) = C^s_A\ C^s_B\ [\ 1 + 8\ (C^s_A\ C^s_B)^2\ ]$$

$$g = \frac{2(\ C_A\ V_A^{2/3} + C_B\ V_B^{2/3}\ )}{n_A^{-1/3} + n_B^{-1/3}}\ cm^2\ du^{1/3}$$

$$C^s_A = \frac{C_A\ V_A^{2/3}}{C_A V_A^{2/3} + C_B\ V_B^{2/3}}$$

$$C^s_B = \frac{C_B\ V_B^{2/3}}{C_A V_A^{2/3} + C_B\ V_B^{2/3}}$$

Where

C^s_A = surface concentration of metal A

C^s_B = surface concentration of metal B

C_A = atomic concentration of metal A

C_B = atomic concentration of metal B

V_A = molar volume of metal A

V_B = molar volume of metal B

n_A = electron density of metal A

n_B = electron density of metal B

on substituting the values of above constraints in proper units the expression for enthalpy reduces to

$$\Delta H = 22.995\ f(C^s)\ g[-p(\Delta\Phi^*)^2 + Q_0(\Delta n_{ws}^{1/3})^2]\ \text{KCals/mole.}$$

2.1) BINARY HYDRIDES:

According to Miedema the metallic hydride is formed in to distinct steps . first, molecular hydrogen is transformed into metallic hydrogen, then the metallic hydrogen is alloyed with transition metal.

2.2) TERNARY HYDRIDES:

Van Mal et al extended the atomic model to the formation of ternary hydrides of the transition metal(AB_nH_{2m}) on the basis of the following assumptions

(a) The hydrogen atom will surround the metal atom of the element,which form a stable binary hydride.

(b) The contact surface area of A-H, and B_n-H is equal. Then ΔH of the ternary hydrides can be written as

$$\Delta H(AB_nH_{2m}) = \Delta H(AH_m) + \Delta H(B_nH_m) - \Delta(AB_n) \qquad \text{(ii)}$$

where

$\Delta H(AH_m)$=Enthalpy of formation of binary hydride of A

$\Delta H(B_nH_m)$=Enthalpy of formation of binary hydride of B_n

$\Delta H(AB_n)$=Enthalpy of formation of original intermetallic compound.

In present work enthalpy of formation was calculated using Fortran programming of the following

(i) Binary intermetallic compounds of the type $Ti_{1-x}M_x$ where M=Fe/Mn/Cr/Ni/V/H and X varies from 0 to 1 with interval of 0.05. (Appendix a.1)

(ii) Binary hydrides of the type $M_{1-x}H_x$ where M=Fe/Mn/Cr/Ni/V/H and X varies from 0 to 1 with interval of 0.05. (Appendix a.2)

(iii) Ternary hydrides TiFeH and $TiFeH_2$. (Appendix a.3)

(iv) Quaternary hydrides of the type $TiFe_{1-x}M_xH$ and $TiFe_{1-x}M_xH_2$ where M=Fe/Mn/Cr/Ni/V/H and X varies from 0 to 1 with interval of 0.05.(Appendix a.4)

Van Mal[1] found experimentally that by replacing 20% of Fe by Mn in TiFe, the activation procedure to form hydride could be made considerably simpler with reference to activation pressure etc. Therefore Mn can be treated as very important addition in Ti-Fe-H system. He also found the replacing part of Fe ,in TiFe by V, Cr, Mn, results in stability of the hydrides.

In present work attempt has been made to depict the effects of the additive metals on a purely theoretical basis.

2.3) COMPUTATION METHOD

The entire calculation of enthalpy of formation is based on the basic equation

$$\Delta H = 22.995\ f(C^{s})\ g[-p(\Delta\Phi^{*})^{2} + Q_{0}(\Delta n_{ws}^{1/3})^{2}]\ \text{KCals/mole.} \quad \text{(ii)}$$

standard values of Q^*, n_{ws}, and V_m were used in the computation. These values for different metals are given in table 2.1[9]. Here hydrogen is considered as an imaginary metal and the values $Q^*=5.05$ V and $n_{ws}=4.6$ du has been assigned to hydrogen metal, which acts as the reference.

a) BINARY INTERMETALLIC COMPOUNDS:

Enthalpy of formation(ΔH) of binary compounds ($Ti_{1-x}M_x$) was calculated for different M(Fe,Mn,Cr,Ni,V,H) and X was taken from 0 to 1 with interval of 0.05. The basic variable in this case is atomic concentration of the metal M. The change in ΔH values due to variation of atomic concentration is given in table 2.2 and the same were plotted in fig 2.1.

b) BINARY HYDRIDES:

ΔH for binary hydrides $M_{1-x}H_x$ was calculated for M=Fe, Mn, Cr, Ni, V, Ti and X=0 to 1 with interval of 0.05. Calculated values are given in table 2.3 and the same are plotted in fig 2.2.

c) TERNARY HYDRIDES:

Enthalpy of formation of ternary hydrides TiFeH and $TiFeH_2$ WAS calculated using equation (ii).Calculated values are

$$\Delta H(TiFeH) = -10.6193 \text{ KCals/mole}$$

$$\Delta H(TiFeH_2) = -20.14448 \text{ KCals/mole}$$

d) QUATERNARY HYDRIDES:

According to Van Mal[4] the enthalpy of formation of quaternary hydrides of the type($TiFe_{1-x}M_xH$) and ($TiFe_{1-x}M_xH_2$) can be expressed as

TABLE 2.1

PARAMETERS FOR THE CALCULATION OF ENTHALPY OF FORMATION OF ALLOYS OF TRANSITION METALS

ELEMENT	Q*	$n_{ws}^{1/3}$ $(du)^{1/3}$	V_m (cm^3)	$V_m^{2/3}$ (cm^2)
Ti	3.65	1.47	10.5	4.8
Fe	4.93	1.77	7.1	3.7
Mn	4.45	1.61	7.4	3.8
Cr	4.65	1.73	7.1	3.7
Ni	5.20	1.75	6.5	3.5
V	4.25	1.64	8.3	4.1
H	5.00	1.66	14.3	5.9

N.B For Li the value of n_{ws} is 1(du), about $6 * 10^{22}$ el/cm^3

TABLE 2.2

CALCULATED ENTHALPY OF FORMATION (In KCals/mole) FOR ($Ti_{1-x}M_x$)

BINARY INTERMETALLIC COMPOUNDS

M = Fe/Mn/Cr/Ni/V/H

ΔH						
X	$Ti_{1-x}H_x$	$Ti_{1-x}Fe_x$	$Ti_{1-x}Mn_x$	$Ti_{1-x}Cr_x$	$Ti_{1-x}Ni_x$	$Ti_{1-x}V_x$
.0000	.0000	.0000	.0000	.0000	.0000	.0000
.0500	-2.2198	-.7724	-.4368	-.3517	-1.5245	-.0921
.1000	-4.4156	-1.5261	-.8631	-.6948	-3.0107	-.1821
.1500	-6.6531	-2.2854	-1.2932	-1.0405	-4.5049	-.2731
.2000	-8.8708	-3.0568	-1.7300	-1.3918	-6.0225	-.3655
.2500	-10.9480	-3.8306	-2.1672	-1.7441	-7.5503	-.4573
.3000	-12.7509	-4.5838	-2.5910	-2.0870	-9.0498	-.5452
.3500	-14.1615	-5.2834	-2.9820	-2.4055	-10.4614	-.6246
.4000	-15.0949	-5.8899	-3.3175	-2.6816	-11.7106	-.6906
.4500	-15.5069	-6.3617	-3.5741	-2.8964	-12.7144	-.7385
.5000	-15.3947	-6.6593	-3.7304	-3.0319	-13.3900	-.7644
.5500	-14.7928	-6.7504	-3.7695	-3.0734	-13.6639	-.7656
.6000	-13.7663	-6.6140	-3.6812	-3.0113	-13.4820	-.7410
.6500	-12.4006	-6.2448	-3.4645	-2.8432	-12.8192	-.6913
.7000	-10.7918	-5.6561	-3.1285	-2.5752	-11.6878	-.6193
.7500	-9.0352	-4.8806	-2.6927	-2.2221	-10.1433	-.5296
.8000	-7.2148	-3.9686	-2.1855	-1.8069	-8.2834	-.4279
.8500	-5.3922	-2.9815	-1.6405	-1.3575	-6.2371	-.3205
.9000	-3.5976	-1.9784	-1.0886	-.9007	-4.1386	-.2128
.9500	-1.8200	-.9934	-.5470	-.4523	-2.0754	-.1071
1.0000	.0000	.0000	.0000	.0000	.0000	.0000

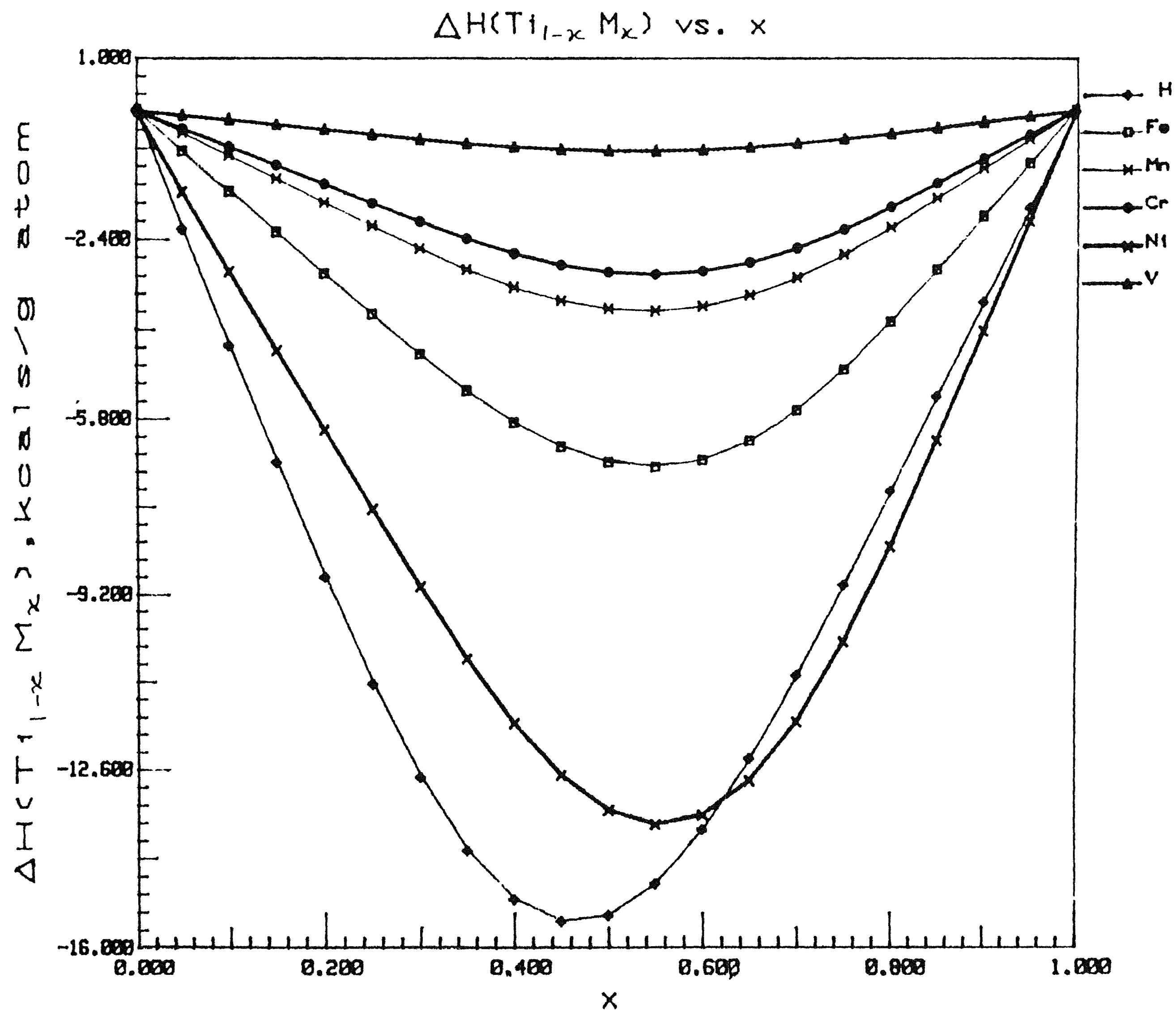

Fig 2.1 PLOT OF ΔH ($Ti_{1-x} M_x$) vs X

TABLE 2.3

CALCULATED ENTHALPY OF FORMATION (In KCals/mole) FOR ($M_{1-x}H_x$) HYDRIDES

M = Ti/Fe/Mn/Cr/Ni/V

	ΔH					
X	$Ti_{1-x}H_x$	$Fe_{1-x}H_x$	$Mn_{1-x}H_x$	$Cr_{1-x}H_x$	$Ni_{1-x}H_x$	$V_{1-x}H_x$
.0000	.0000	.0000	.0000	.0000	.0000	.0000
.0500	-2.2198	.1783	-.4363	-.1239	.0589	-.8828
.1000	-4.4156	.3568	-.8724	-.2478	.1179	-1.7622
.1500	-6.6531	.5370	-1.3135	-.3730	.1772	-2.6552
.2000	-8.8708	.7076	-1.7339	-.4915	.2326	-3.5194
.2500	-10.9480	.8554	-2.1016	-.5941	.2795	-4.2949
.3000	-12.7509	.9699	-2.3905	-.6736	.3146	-4.9269
.3500	-14.1615	1.0451	-2.5848	-.7259	.3365	-5.3768
.4000	-15.0949	1.0795	-2.6790	-.7498	.3451	-5.6254
.4500	-15.5069	1.0752	-2.6770	-.7468	.3414	-5.6722
.5000	-15.3947	1.0370	-2.5892	-.7202	.3272	-5.5320
.5500	-14.7928	.9710	-2.4305	-.6744	.3049	-5.2306
.6000	-13.7663	.8841	-2.2175	-.6141	.2765	-4.8004
.6500	-12.4006	.7830	-1.9667	-.5438	.2442	-4.2765
.7000	-10.7918	.6735	-1.6932	-.4678	.2097	-3.6924
.7500	-9.0352	.5604	-1.4093	-.3892	.1744	-3.0776
.8000	-7.2148	.4469	-1.1239	-.3104	.1391	-2.4544
.8500	-5.3922	.3348	-.8417	-.2325	.1043	-1.8366
.9000	-3.5976	.2242	-.5634	-.1557	.0699	-1.2282
.9500	-1.8200	.1136	-.2855	-.0789	.0354	-.6221
1.0000	.0000	.0000	.0000	.0000	.0000	.0000

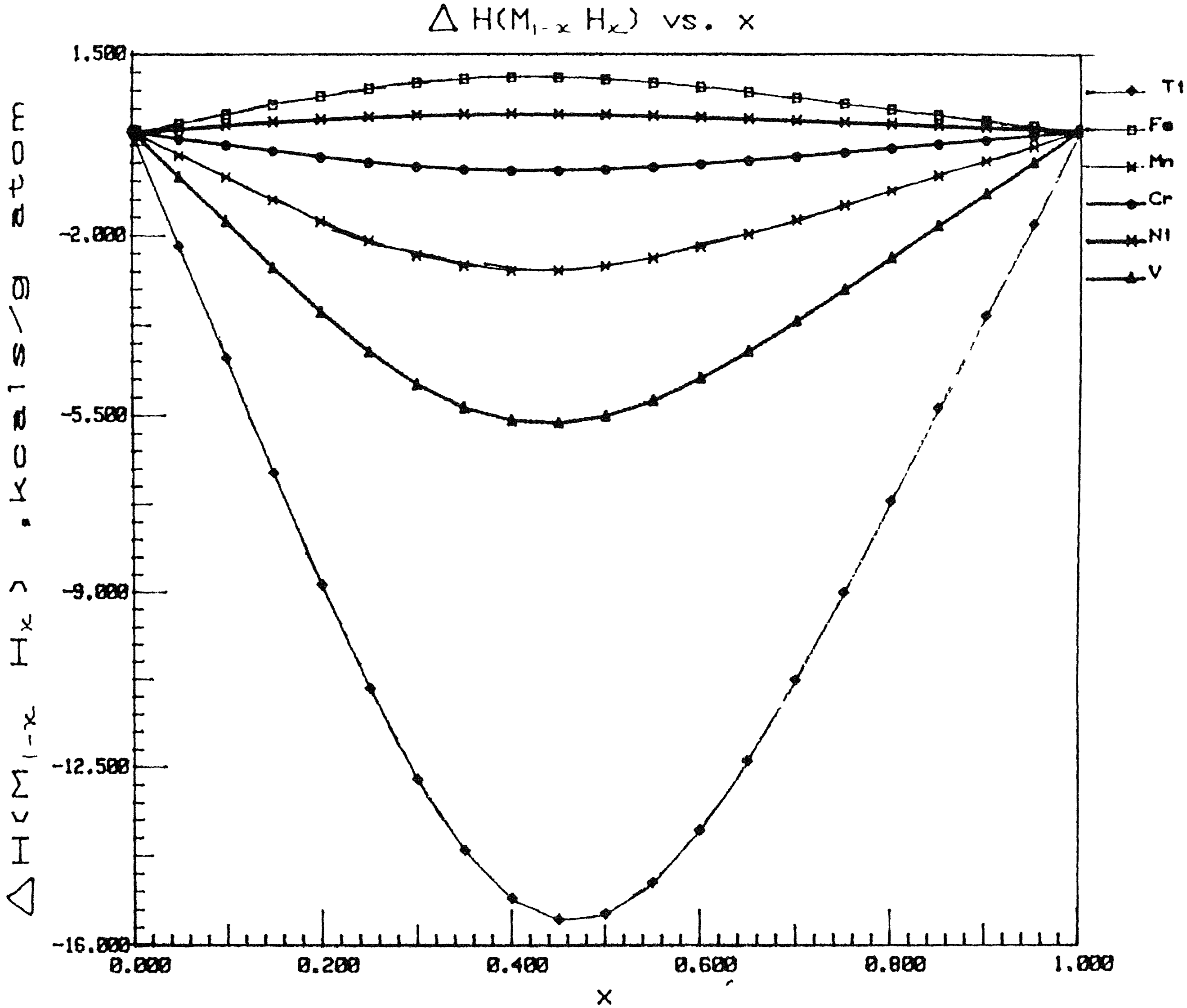

Fig 2.2 PLOT OF ΔH (M_{1-x} H_x) vs X

$$\Delta H(TiFe_{1-x}M_xH) = \Delta H(TiH_{0.5}) + \Delta H(Fe_{1-x}M_xH_{0.5}) - \Delta H(TiFe_{1-x}M_x)$$

$$= \Delta H(TiH_{0.5}) + [\ \Delta H(Fe_{1-x}H_{0.25}) + \Delta H(M_xH_{0.25}) - \Delta H(Fe_{1-x}M_x)] - [\ \Delta H(Ti_{0.5}Fe_{1-x}) + \Delta H(Ti_{0.5}M_x)]$$

similarly

$$\Delta H(TiFe_{1-x}M_xH_2) = \Delta H(TiH) + [\ \Delta H(Fe_{1-x}H_{0.5}) + \Delta H(M_xH_{0.5}) - \Delta H(Fe_{1-x}M_x)] - [\ \Delta H(Ti_{0.5}Fe_{1-x}) + \Delta H(Ti_{0.5}M_x)]$$

For different M=Mn/Cr/Ni/V and X=0 to 1 with interval of 0.05 enthalpy of quaternary hydrides were calculated.The variation in ΔH values with x are given in table 2.4, 2.5 for $TiFe_{1-x}M_xH$ and $TiFe_{1-x}M_xH_2$ respectively and same are plotted in fig 2.3 and 2.4.

2.4) RESULTS AND DISCUSSION

Fig 2.1 shows that the all the curves are in negative ΔH region. Hence for all the systems, formation of binary intermetallic compounds is possible. Stability of the various systems can be described in decreasing order as Ti-H > Ti-Ni > Ti-Fe > Ti-Mn > Ti-Cr > Ti-V. The stability of Ti-Ni is slightly greater than that of Ti-H system beyond the atomic fraction of 0.6 . Atomic fraction of different for which ΔH is minimum (stability is maximum) is different.

Fig 2.2 shows that formation of binary hydrides of Ni and Fe is not stable as ΔH is positive in most of the composition range. Stability of other binary hydrides in the decreasing order can be

TABLE 2.4

CALCULATED ENTHALPY OF FORMATION (In KCals/mole) FOR ($TiFe_{1-x}M_xH$) COMPOUNDS

M = Mn/Cr/Ni/V

ΔH				
X	$TiFe_{1-x}Mn_xH$	$TiFe_{1-x}Cr_xH$	$TiFe_{1-x}Ni_xH$	$TiFe_{1-x}V_xH$
.0000	-10.6193	-10.6193	-10.6193	-10.6193
.0500	-10.6088	-10.4123	-9.1380	-10.9252
.1000	-10.6215	-10.2277	-7.6866	-11.2616
.1500	-10.6399	-10.0561	-6.2326	-11.5809
.2000	-10.6612	-9.9052	-4.8137	-11.8544
.2500	-10.6939	-9.7887	-3.4764	-12.0915
.3000	-10.7504	-9.7208	-2.2588	-12.3213
.3500	-10.8428	-9.7145	-1.1880	-12.5788
.4000	-10.9818	-9.7809	-.2810	-12.8967
.4500	-11.1761	-9.9290	.4522	-13.3020
.5000	-11.4336	-10.1662	1.0072	-13.8139
.5500	-11.7608	-10.4979	1.3832	-14.4437
.6000	-12.1634	-10.9275	1.5829	-15.1952
.6500	-12.6454	-11.4560	1.6118	-16.0648
.7000	-13.2087	-12.0812	1.4788	-17.0429
.7500	-13.8509	-12.7964	1.1973	-18.1135
.8000	-14.5642	-13.5888	.7865	-19.2550
.8500	-15.3318	-14.4380	.2732	-20.4398
.9000	-16.1280	-15.3152	-.3083	-21.6361
.9500	-16.9250	-16.1918	-.9243	-22.8179
1.0000	-17.7312	-17.0791	-1.5822	-24.0063

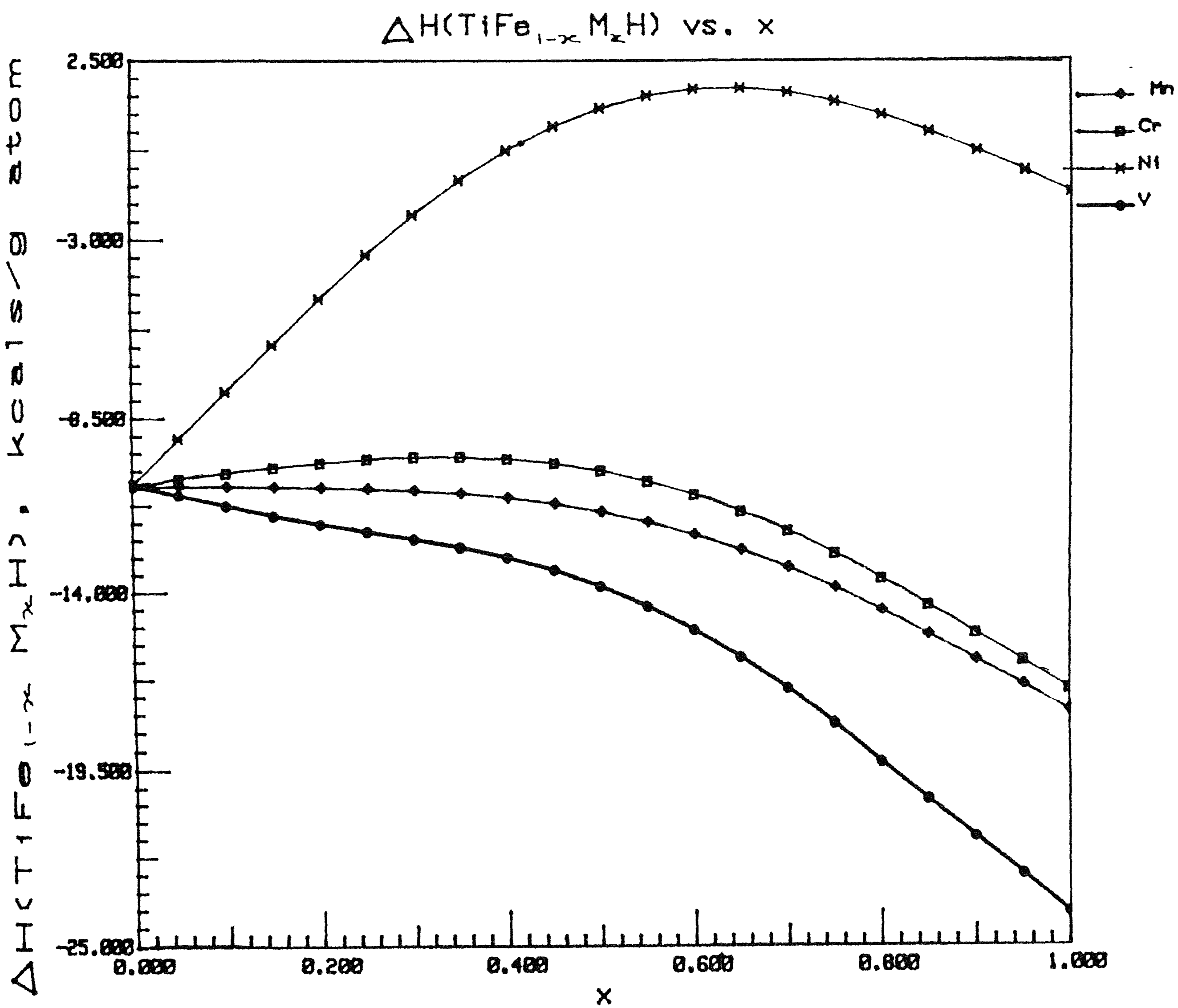

Fig 2.3 PLOT OF ΔH ($TiFe_{1-x}$ M_xH) vs X

TABLE 2.5

CALCULATED ENTHALPY OF FORMATION (In KCals/mole) FOR ($TiFe_{1-x}M_xH_2$) COMPOUNDS

M = Mn/Cr/Ni/V

	ΔH			
X	$TiFe_{1-x}Mn_xH_2$	$TiFe_{1-x}Cr_xH_2$	$TiFe_{1-x}Ni_xH_2$	$TiFe_{1-x}V_xH_2$
.0000	-20.1448	-20.1448	-20.1448	-20.1448
.0500	-20.1624	-19.9648	-18.6898	-20.4797
.1000	-20.1992	-19.8077	-17.2679	-20.8359
.1500	-20.2587	-19.6699	-15.8449	-21.2189
.2000	-20.3527	-19.5631	-14.4567	-21.6295
.2500	-20.4912	-19.5017	-13.1493	-22.0746
.3000	-20.6812	-19.4987	-11.9614	-22.5669
.3500	-20.9273	-19.5652	-10.9207	-23.1224
.4000	-21.2329	-19.7100	-10.0448	-23.7576
.4500	-21.6008	-19.9405	-9.3441	-24.4865
.5000	-22.0339	-20.2621	-8.8230	-25.3188
.5500	-22.5347	-20.6784	-8.4816	-26.2591
.6000	-23.1054	-21.1910	-8.3165	-27.3060
.6500	-23.7470	-21.7987	-8.3205	-28.4524
.7000	-24.4583	-22.4966	-8.4826	-29.6854
.7500	-25.2341	-23.2755	-8.7868	-30.9864
.8000	-26.0635	-24.1197	-9.2112	-32.3314
.8500	-26.9282	-25.0068	-9.7272	-33.6917
.9000	-27.8037	-25.9090	-10.3011	-35.0374
.9500	-28.6681	-26.8038	-10.9053	-36.3494
1.0000	-29.5384	-27.7101	-11.5548	-37.6579

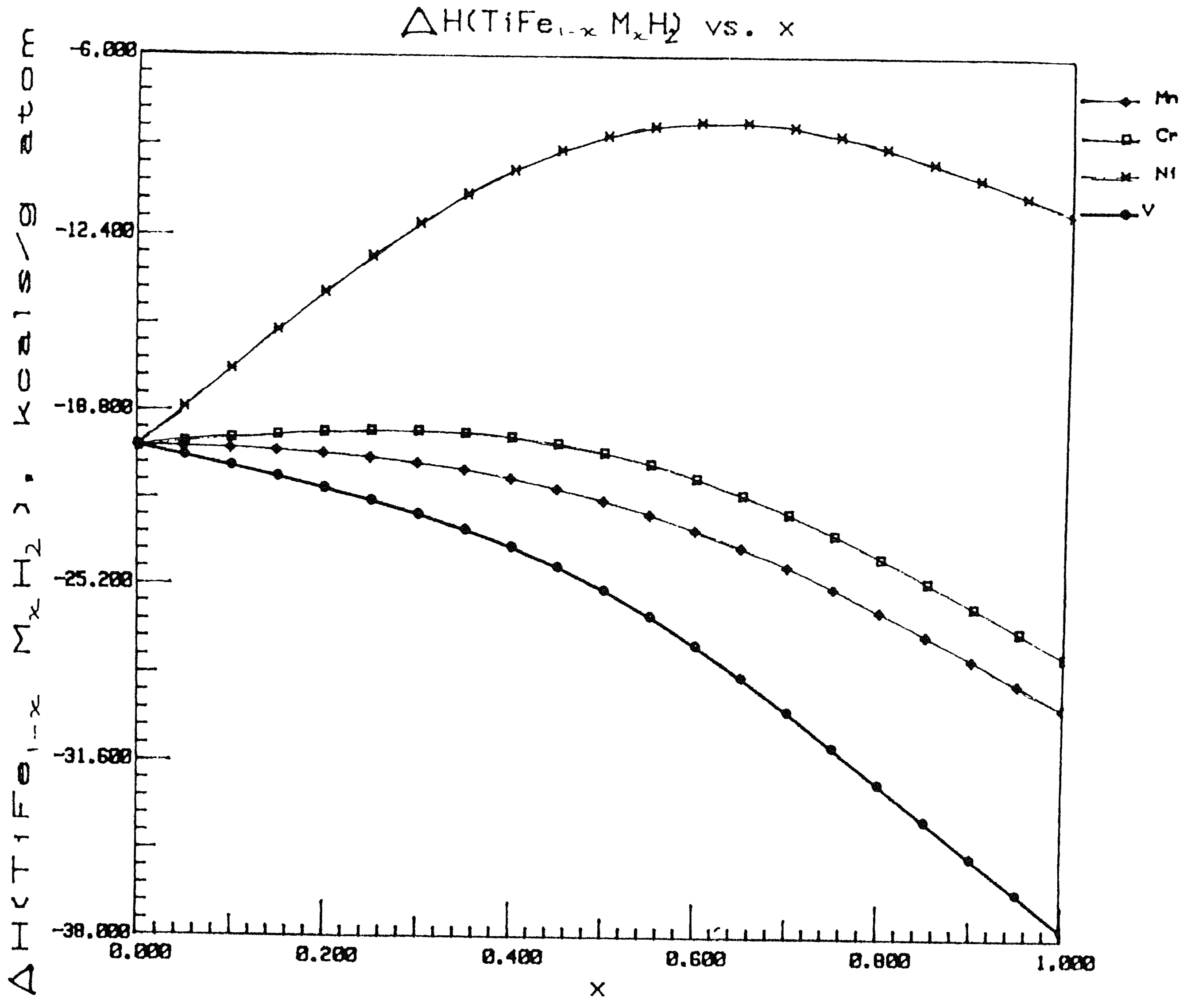

Fig 2.4 PLOT OF ΔH ($TiFe_{1-x}M_xH_2$) vs X

described as Ti-H > V-H > Mn-H > Cr-H .

Fig 2.3 and 2.4 show that $TiFe_{1-x}M_xH$ and $TiFe_{1-x}M_xH_2$ systems partial replacement Fe by other transition metals (Mn,Cr,Ni,V etc.) gives pronounced effect on the stability .

In $TiFe_{1-x}M_xH$ system, ΔH is confined in negative zone for M = Mn, Cr, V where as for M=Ni, the enthalpy changes sign from negative to positive values over the composition range twice. Hence stability of $TiFe_{1-x}M_xH$ first decreases up to atomic fraction x=0.4 , after that it assumes positive sign up to x=0.88 after which it again becomes negative slowly. Stability of $TiFe_{1-x}Mn_xH$ and $TiFe_{1-x}V_xH$ first increases slowly up to x=0.5, after that stability increases very fast.For $TiFe_{1-x}Cr_xH$ stability decreases very slowly up to x=0.5 ,after that it increases very fast. The stability of the different systems in decreasing order can be written as $TiFe_{1-x}V_xH$ > $TiFe_{1-x}Mn_xH$ > $TiFe_{1-x}Cr_xH$.

Fig 2.4 gives the plot of $TiFe_{1-x}M_xH_2$ for different x. The shape of the curves for different M is same as that of $TiFe_{1-x}M_xH$ system. The only difference is that all the curves are in negative ΔH zone. Hence formation of all stable hydrides is possible. for M= Ni, the stability first decreases up to X=0.52 , after that it increases. For $TiFe_{1-x}V_xH_2$ and $TiFe_{1-x}Mn_xH_2$ stability increases slowly up to X=0.4 after that it increases very fast. The stability of different systems in decreasing order can be described as $TiFe_{1-x}V_xH_2$ > $TiFe_{1-x}Mn_xH_2$ > $TiFe_{1-x}Cr_xH_2$ > $TiFe_{1-x}Ni_xH_2$. Hence one can see that relative stability of the different hydrides is same in both the system.

CHAPTER 3

APPLICATION OF METAL HYDRIDES IN HEAT PUMPING

ABSTRACT:

Hydriding of intermetallic releases heat energy and dissociation of intermetallic hydrides absorbs heat energy as these reactions are exothermic and endothermic .The heat of reaction ΔH is related to pressure of reaction (absorption/desorption) thermodynamically by the relation $\ln p=\Delta H/RT -\Delta S/R$[1]

Thus it is possible to utilize this reaction for various heat pumping application. In the present chapter the principle of heat pumping for cooling is discussed and calculation for $MmNi_{5-x}Mn_xH_\delta$[40] type metal hydride system developed indigenously done.

The thermal energy involved in absorption and desorption and desorption process makes it possible with appropriate combination of metal -hydrogen system ,to use it at a high temperature for pumping heat from a low temperature source and vice-versa.This process can be thus used both for cooling and for heating applications.

For metal hydrides the equilibrium pressure in the two phase region varies strongly with temperature and represented by

$$\ln p=\Delta H/RT -\Delta S/R$$ [1]

where

ΔH= Heat of hydride formation (Cal/ mole of H_2)

p= the pressure at which hydride is formed (atm)

ΔS= Change in entropy during hydride formation (Cal/mole^{o}k)

ΔS is equal for all metal -hydrogen system and constant in small temperature range considered and also ΔH is independent of temperature, the effect of temperature and hydriding pressure of a metal -hydrogen system is represented graphically by fig 3.1[4]. This shows the plots of $\ln p_{H_2}$ VS $1/T$ for different systems. All straight lines converge to the point $\ln p_{H_2} = -\Delta S/R$on the line $1/T=0$. This representation helps in finding the characteristics ΔH of a particular metal-hydrogen system, required for heat pumping.

A metal hydride heat pump consists of two hydrides with dissimilar thermal stabilities situated in different sections of a sealed container, such that hydrogen gas can flow freely from one section to the other. Fig 3.2[5]illustrates heat pump operation in cooling mode. Cooling is a result of the dissociation of less stable hydride M_2H_Y(endothermic reaction) at point A. The dissociated hydrogen flows from point A to the initially hydrogen depleted M_1 at point B to form more stable hydride M_1H_x.Low temperature hydride absorb heat from the air. By holding M_1H_xat T_m(i.e. maintained at ambient temperature by removing absorption heat), P_2will be greater than $P_1$and hydrogen will flow from A to B and the low temperature will be maintained. When the hydrogen content of M_2H_X has been exhausted, it is regenerated by allowing it to return to temperature T_m and contacting with H_2 after heating M_1H_x toT_H (e.g. using industrial waste heat, solar energy etc which liberates H_2) at point C. Thus hydrogen will flow back to the hydrogen depleted M_2(along C-D) since $P_4 > P_3$.By operating an identical two-hydride system in tandem, continuous cooling is obtained.The line sketch of proposed system is given in Fig3.3[2].

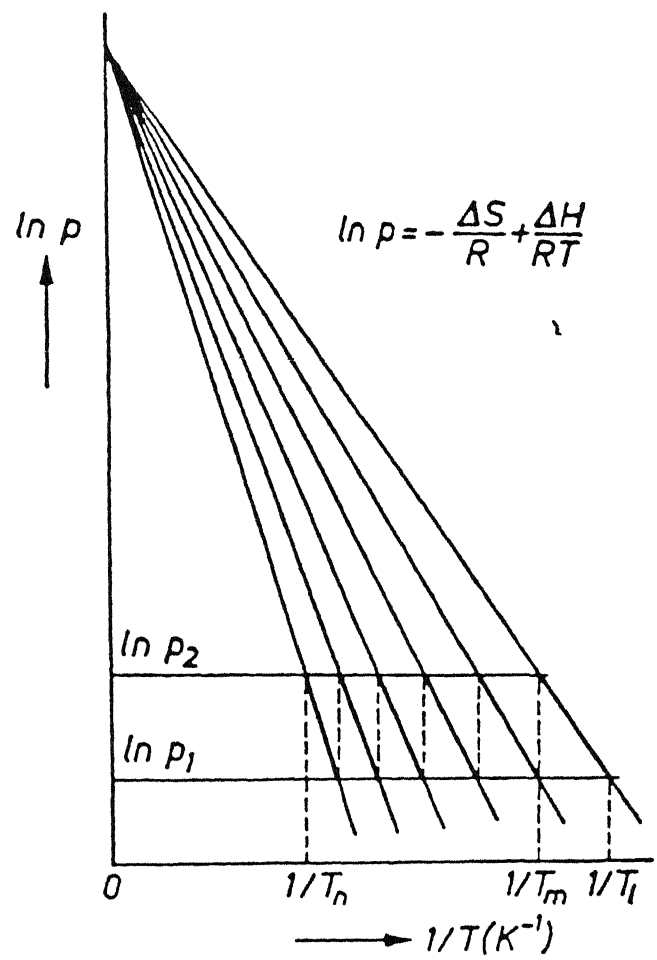

Fig 3.1 PLOT OF ln p_{H_2} VS 1 / T FOR DIFFERENT SYSTEMS

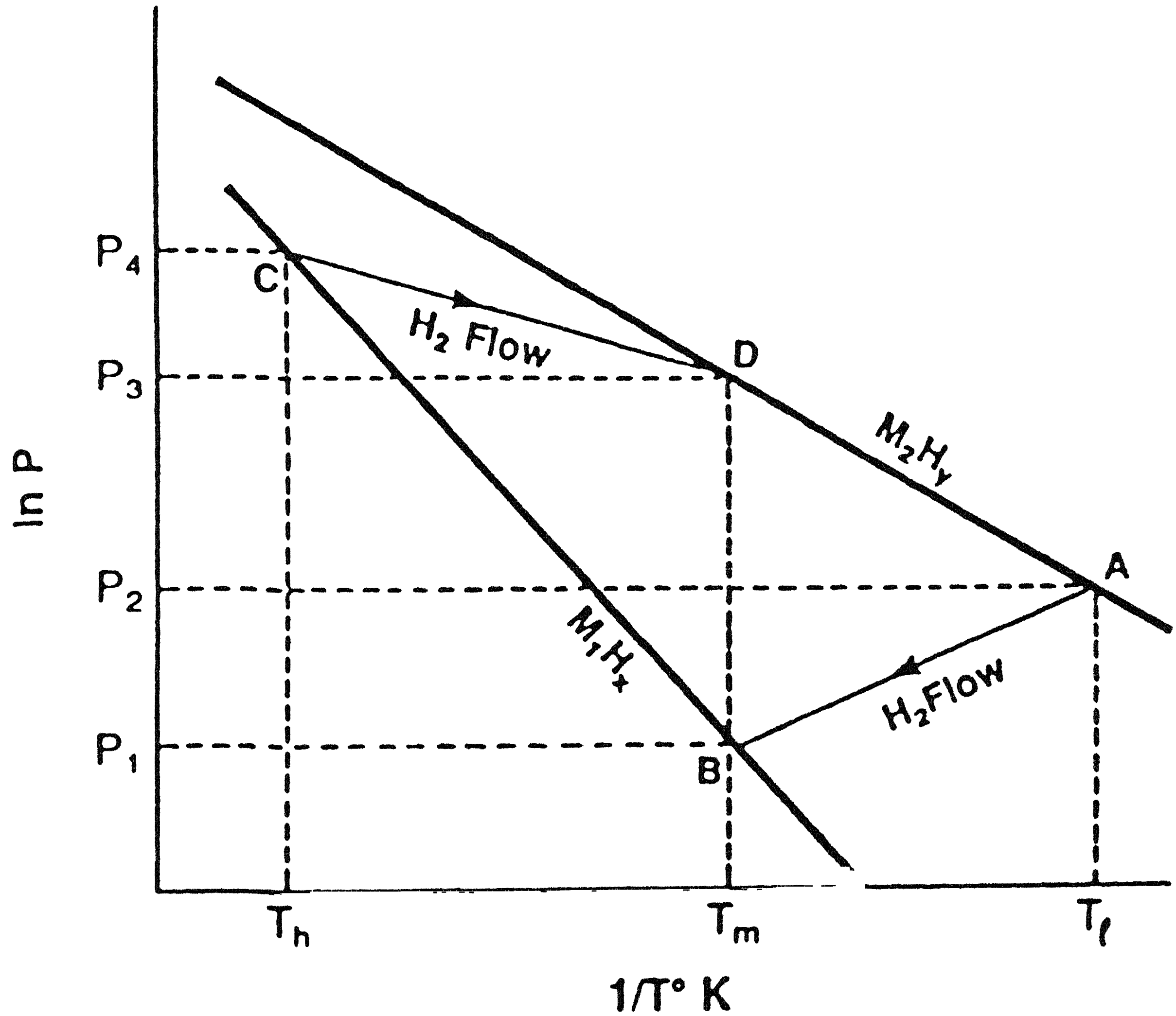

Fig 3.2 OPERATION OF METAL HYDRIDE HEAT PUMP IN THE COOLING MODE

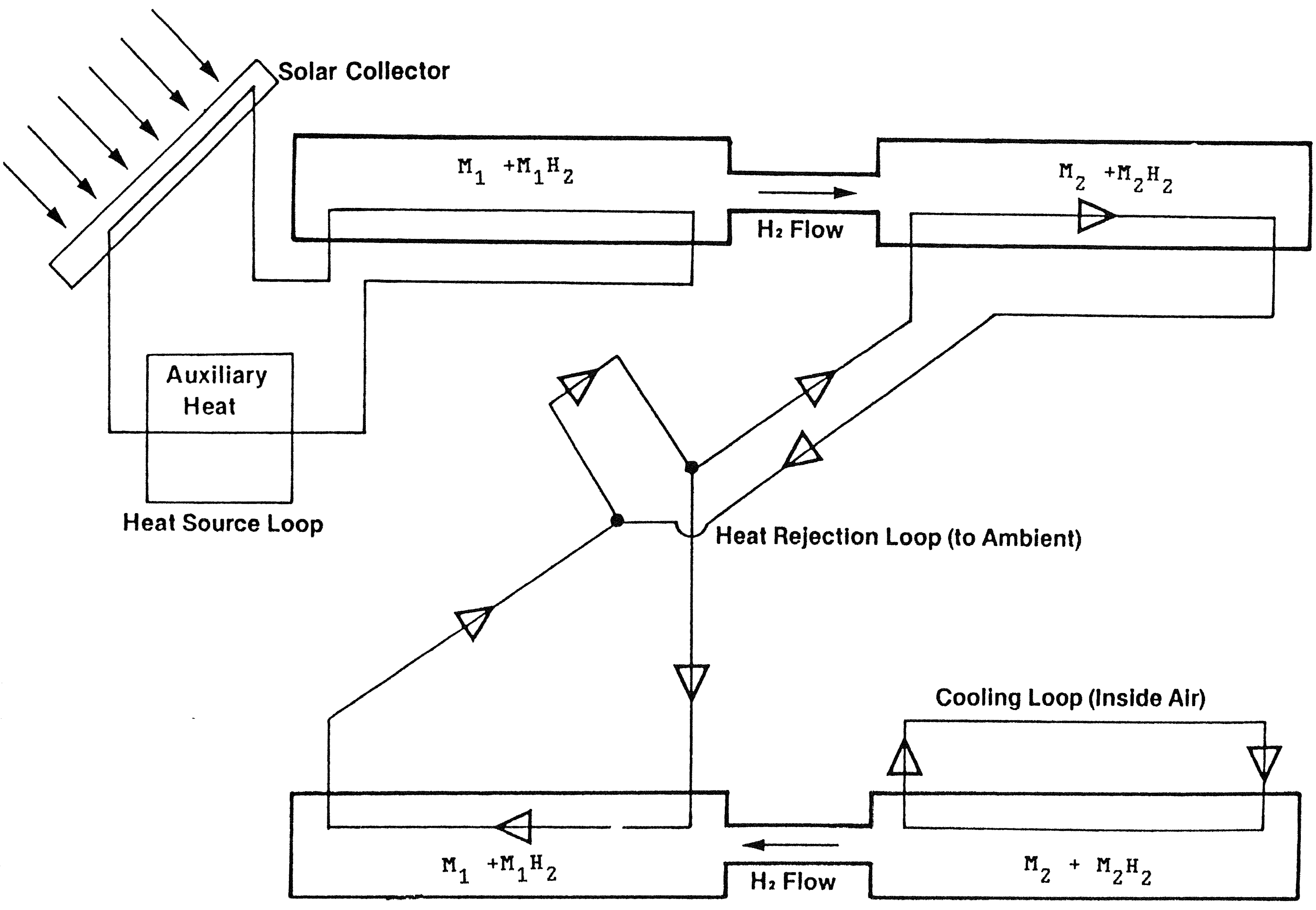

Fig 3.3 SCHEMATIC DIAGRAM OF HYDRIDE HEAT PUMP IN ONE CYCLE OF COOLING MODE

The theoretical maximum COP of the hydride based heat pump is given by $\Delta H_2/\Delta H_1$[5]

where ΔH_1 = enthalpy of formation of more stable hydride and

ΔH_2 = enthalpy of formation of less stable hydride.

In Metal Hydride heat pumping utilizing AB_5 type of hydrides ΔH_2 is always lower (magnitude of negative value) than ΔH_1 in order to maintain hydrogen flow from A to B (Fig 3.2[5]) as the dissociation pressure of M_2H_y is higher than that of M_1H_x. Since the ΔS value for both the hydrides are about the same, this can be accomplished if ΔH_1 is more negative (higher absolute value) than ΔH_2. As a result maximum value of the COP is always less than unity. The operating temperatures of a metal hydrides heat pump are dependent on the enthalpies (ΔH) of the hydrides chosen for the system.

As already noted above, the operating temperatures of a metal hydride heat pump are determined by the enthalpies (ΔH) of the pair of hydrides chosen for the system. One of the great assets of the hydride heat pump is large range of enthalpies for different metal hydrides. The large number of hydrides allow the system to be selected to meet the heating and cooling needs of the user. Further, the enthalpies of ternary alloys can be varied over a small range by varying the composition of the alloy, allowing for a fine tuning of the heat pump.

The main advantages of the hydride based heat pumps are that these are pollution free and can use low grade energy. By proper choice of two hydrides even compressor can be eliminated.

CHAPTER 4

DESIGN CALCULATIONS BASED ON Mm $Ni_{4.2}$ $Mn_{0.8}$ and Mm $Ni_{4.2}$ $Al_{0.8}$ INTERMETALLICS FOR HEAT PUMPING APPLICATIONS

The two indigenously developed intermetallics[10] using Indian Mischmetal are $MmNi_{4.2}Mn_{0.8}$ and $MmNi_{4.2}Al_{0.8}$. Their thermodynamic parameters evaluated by Mangole et al[10] are

$\Delta H_{desorption}$ for $MmNi_{4.2}Mn_{0.8}H_y$ = 28.40 kJ/mole of H_2 = ΔH_2

$\Delta H_{absorption}$ for $MmNi_{4.2}Al_{0.8}H_y$ = 32.36 kJ/mole of H_2 = ΔH_1 .

Hydrogen to metal ratio for both cases H/M = 0.3

Let us assume that absorption/desorption reactions take 10 minutes to complete up to 90% capacity of metal hydride.

4.1) COST CALCULATIONS :

Due to desorption of $MmNi_{4.2}Mn_{0.8}H_y$ cooling effect per second, $\Delta H_2' = \frac{28.40 * 0.9}{60 * 10} = 0.423$ kW/mole of H_2

Now for 1 ton = 3.5 kW of cooling total moles of H_2 required =

$$\frac{\text{Total cooling}}{\text{Cooling/mole of } H_2} = \frac{1 \text{ ton}}{\Delta H_2'} = \frac{3.5 \text{ kW}}{0.09 \text{ kw/mole}} \simeq 81 \text{ mole}$$

Hence metal required for 1 ton of cooling

$$= \frac{\text{Hydrogen}}{0.3} = \frac{81}{0.3} \simeq 270 \text{ moles}$$

$\rightarrow$ weight of hydride required for 1 ton of cooling = $W_{H_2} + W_M$

$$= 81 * 2 + 270 * 248.3 = 67203 \text{ gm} \simeq 67 \text{ kg}$$

Now weight of metal M_1 required = 270 * 243.3 = 65691 gm $\simeq$ 66 kgAssuming cost of both the metal and metal hydride = Rs. 500/kg

Installation cost, pipe, etc. = Rs. 10,000 /-

→ Total cost = Material cost + Installation cost

= [500 (66 + 67)] + 10000

= Rs. 76,500 /-

4.2) COP CALCULATIONS :

Coefficient of Performance of the cycle is given by[5]

$$COP = \Delta H_2 / \Delta H_1 = \frac{28.40}{92.96} = 0.877$$

APPENDIX

a.1) FORTRAN PROGRAMME USED TO CALCULATE ENTHALPY OF FORMATION OF $(Ti_{1-x}M_x)$ SYSTEM

```
      print4
4     format (78('_'))
      x=0.000000000001
      hh=h(x,14.3,1.66,5.00)
      hfe=h(x,7.1,1.77,4.93)
      hmn=h(x,7.4,1.61,4.45)
      hcr=h(x,7.1,1.73,4.65)
      hni=h(x,6.5,1.75,5.2)
      hv=h(x,8.3,1.64,4.25)
      print6,x,hh,hfe,hmn,hcr,hni,hv
6     format ('|',7(F8.4,2X,'|'))
      x=0.0
      do 10 i=1,20
      x=x+0.05
      hh=h(x,14.3,1.66,5.00)
      hfe=h(x,7.1,1.77,4.93)
      hmn=h(x,7.4,1.61,4.45)
      hcr=h(x,7.1,1.73,4.65)
      hni=h(x,6.5,1.75,5.2)
      hv=h(x,8.3,1.64,4.25)
      print5,x,hh,hfe,hmn,hcr,hni,hv
5     format ('|',7(F8.4,2X,'|'))
10    continue
      print7
7     format (78('-'))
      stop
      end

      function h(cb,vb,nb,qb)
      real h,f,cas,cbs,g,ca,cb,va,vb,na,nb,p,qa,qb,q
      ca=1-cb
      va=10.5
```

```
na=1.47
qa=3.65
g=2*(ca*va**.6667+cb*vb**.6667)/(na**(-1)+nb**(-1))
ca1= ca*(va**.6667)
ca2= ca*va**.6667+cb*vb**.6667
cas= ca1/ca2
cbs=cb*vb**.6667*cas/(ca*va**.6667)
f=cas*cbs*(1+8*(cas*cbs)**2)
p=0.147
q=p*9.4
h=22.9995*f*g*(-p*(qb-qa)**2+q*(nb-na)**2)
return
end
```

a.2) FORTRAN PROGRAMME USED TO CALCULATE ENTHALPY OF FORMATION OF ($M_{1-x}H_x$) SYSTEM

```
      print8
8      format(78('_'))
       x=0.00000001
       hti=h(x,10.5,1.47,3.65)
       hfe=h(x,7.1,1.77,4.93)
       hmn=h(x,7.4,1.61,4.45)
       hcr=h(x,7.1,1.73,4.65)
       hni=h(x,6.5,1.75,5.2)
       hv=h(x,8.3,1.64,4.25)
       print7,x,hti,hfe,hmn,hcr,hni,hv
7      format ('|', 7(F8.4,2X,'|'))
       x=0.0
       do 10 i=1,20
       x=x+0.05
       hti=h(x,10.5,1.47,3.65)
       hfe=h(x,7.1,1.77,4.93)
       hmn=h(x,7.4,1.61,4.45)
       hcr=h(x,7.1,1.73,4.65)
       hni=h(x,6.5,1.75,5.2)
       hv=h(x,8.3,1.64,4.25)
       print5,x,hti,hfe,hmn,hcr,hni,hv
5      format ('|',7(F8.4,2X,'|'))
10     continue
c       print* (60('-'))
       print9
9      format(78('-'))
       stop
       end

       function h(cb,va,na,qa)
       real h,f,cas,cbs,g,ca,cb,va,vb,na,nb,p,qa,qb,q
       ca=1-cb
       vb=14.3
       nb=1.66
       qb=5
```

```
g=2*(ca*va**.6667+cb*vb**.6667)/(na**(-1)+nb**(-1))
ca1= ca*(va**.6667)
ca2= ca*va**.6667+cb*vb**.6667
cas= ca1/ca2
cbs=cb*vb**.6667*cas/(ca*va**.6667)
f=cas*cbs*(1+8*(cas*cbs)**2)
p=0.147
q=p*9.4
h=22.9995*f*g*(-p*(qb-qa)**2+q*(nb-na)**2)
return
end
```

a.3) FORTRAN PROGRAMME USED TO CALCULATE ENTHALPY OF FORMATION OF ($TiFe_{1-x}M_xH$) SYSTEM

```
      print4
4     format(69('_'))
      x=0.00000001
      hhmn=hh(x,7.4,1.61,4.45)
      hhcr=hh(x,7.1,1.73,4.65)
      hhni=hh(x,6.5,1.75,5.20)
      hhv=hh(x,8.3,1.64,4.25)
      print5,x,hhmn,hhcr,hhni,hhv
5     format('|',5(F8.4,3X,'|   '))
      x=0.0
      do 10 i=1,20
      x=x+0.05
      hhmn=hh(x,7.4,1.61,4.45)
      hhcr=hh(x,7.1,1.73,4.65)
      hhni=hh(x,6.5,1.75,5.20)
      hhv=hh(x,8.3,1.64,4.25)
      print6,x,hhmn,hhcr,hhni,hhv
6     format('|',5(F8.4,3X,'|   '))
10    continue
      print7
7     format(69('-'))
      stop
      end

      function hh(x,v,n,q)
      real n
      h1=h(1.0,0.5,10.5,14.3,1.47,1.66,3.65,5.00)
      h2=h((1-x),0.25,7.1,14.3,1.77,1.66,4.93,5.00)
      h3=h(0.5,(1-x),10.5,7.1,1.47,1.77,3.65,4.93)
      h4=h(x,0.25,v,14.3,n,1.66,q,5.00)
      h5=h((1-x),x,7.1,v,1.77,n,4.93,q)
      h6=h(0.5,x,10.5,v,1.47,n,3.65,q)
      hh=h1+h2+h4-h5-h3-h6
      return
```

```
end

function h(ca,cb,va,vb,na,nb,qa,qb)
real h,f,cas,cbs,g,ca,cb,va,vb,na,nb,p,qa,qb,q
g=2*(ca*va**.6667+cb*vb**.6667)/(na**(-1)+nb**(-1))
ca1= ca*(va**.6667)
ca2= ca*va**.6667+cb*vb**.6667
cas= ca1/ca2
cbs=cb*vb**.6667*cas/(ca*va**.6667)
f=cas*cbs*(1+8*(cas*cbs)**2)
p=0.147
q=p*9.4
h=22.9995*f*g*(-p*(qb-qa)**2+q*(nb-na)**2)
return
end
```

a.4) FORTRAN PROGRAMME USED TO CALCULATE ENTHALPY OF FORMATION

OF ($TiFe_{1-x}M_xH_2$) SYSTEM

```
      print4
4     format(69('_'))
      x=0.00000001
      hhmn=hh(x,7.4,1.61,4.45)
      hhcr=hh(x,7.1,1.73,4.65)
      hhni=hh(x,6.5,1.75,5.20)
      hhv=hh(x,8.3,1.64,4.25)
      print5,x,hhmn,hhcr,hhni,hhv
5     format('|',5(F8.4,3X,'|   '))
      x=0.0
      do 10 i=1,20
      x=x+0.05
      hhmn=hh(x,7.4,1.61,4.45)
      hhcr=hh(x,7.1,1.73,4.65)
      hhni=hh(x,6.5,1.75,5.20)
      hhv=hh(x,8.3,1.64,4.25)
      print6,x,hhmn,hhcr,hhni,hhv
6     format('|',5(F8.4,3X,'|   '))
10    continue
      print7
7     format(69('-'))
      stop
      end

      function hh(x,v,n,q)
      real n
      h1=h(1.0,1.0,10.5,14.3,1.47,1.66,3.65,5.00)
      h2=h((1-x),0.5,7.1,14.3,1.77,1.66,4.93,5.00)
      h3=h(0.5,(1-x),10.5,7.1,1.47,1.77,3.65,4.93)
      h4=h(x,0.5,v,14.3,n,1.66,q,5.00)
      h5=h((1-x),x,7.1,v,1.77,n,4.93,q)
      h6=h(0.5,x,10.5,v,1.47,n,3.65,q)
      hh=h1+h2+h4-h5-h3-h6
      return
```

```
end
function h(ca,cb,va,vb,na,nb,qa,qb)
real h,f,cas,cbs,g,ca,cb,va,vb,na,nb,p,qa,qb,q
g=2*(ca*va**.6667+cb*vb**.6667)/(na**(-1)+nb**(-1))
ca1= ca*(va**.6667)
ca2= ca*va**.6667+cb*vb**.6667
cas= ca1/ca2
cbs=cb*vb**.6667*cas/(ca*va**.6667)
f=cas*cbs*(1+8*(cas*cbs)**2)
p=0.147
q=p*9.4
h=22.9995*f*g*(-p*(qb-qa)**2+q*(nb-na)**2)
return
end
```

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